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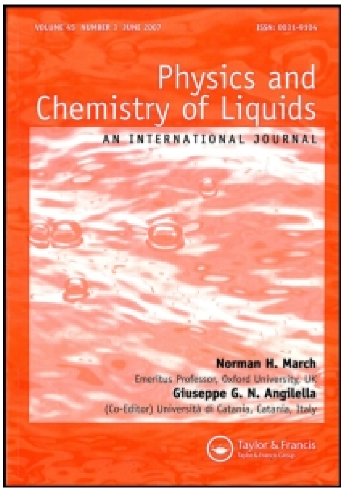

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Fluid-Fluid Phase Separation by Molecular Dynamics

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Miscibility of several binary fluid systems, placed in an external gravitational field, has been studied by Molecular Dynamics calculation. The results show inmiscibility and phase separation to appear as a consequence of differences in the Lennard-Jones energy parameter of molecular interaction. Two situations are primarily considered: The case of a big difference in the energy parameters of pure components and the case of a weak interaction between unlike molecules.

INTRODUCTION

Partial miscibility of pure fluids, in the same way as liquid-vapour phase transition for pure components, is only possible in the case of attractive molecular potentials.[1]

On the other hand, excess properties of fluid binary mixtures are primarily dependent, from the molecular point of view, on differences in the attractive potential of the components and only secondarily on differences in molecular size.[2] In extreme cases these differences in intermolecular potentials yield a separation into two phases at a given Temperature and volumen when the stability criterion $(d^2A/dx^2)_{T,V} \geq 0$ (with A, the Helmholtz function of the mixture, and x, the molar fraction of one component) is violated. If an external gravitational field is present, a spatial distribution of the phases occurs, according to the average molecular weight of both.[3]

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Phase separation for simple fluid systems occurs not only in several well-known liquid mixtures[4] (systems with upper consolute Temperature in their phase diagram), but also in some gas mixtures above the critical point at enough high pressure.[5]

Simulation by computer studies about mixtures have been centered on thermodynamic properties of almost ideal systems,[6] but the specific problem of phase separation has received few attention.[7] The related problems of liquid-vapour phase transition, free surface structure and surface tension have received increasing attention in the last few years for both pure components[8] and mixtures.[9]

There are several questions, still unanswered in simple liquid mixtures that can be addressed, but we have attended just to the following:

Under what microscopic conditions a two liquid phase separation, assisted by an external gravitational field, takes place? Previous work in this area has been polarized between formal[3,10] and observational[3–5] approaches, and we believe it may be susceptible to an inductive attack such as is provided by simulation methods. Despite the apparent simplicity of this task, there are many practical difficulties we have to overcome in some cases or to avoid in others. First of all, we are dealing with a non-equilibrium phenomenon and consequently we need the non-equilibrium Molecular Dynamics methods.[11] Secondly, the kinematic description of phase separation leads to the problem of cluster formation and nucleation theory.[12] We have to avoid also the critical region because in such situation the correlations extend further than our simulated sample length. Last, the gravitational field, on the one hand introduces a privileged direction so as to make useless the periodic boundary conditions of the simulation method (being necessary the introduction of walls that, as a counterpart, creates oscillation in the fluid density near them), and on the other, acting as a secular effect, produces almost inappreciable changes during the small time interval of the entire simulation.[13]

In order to gain some insight into this problem, and without losing generality we have used some simplifications. We work with simple structureless Lennard-Jones molecules, i.e. systems with lower consolute Temperature are not considered. The gravitational field is very large; the average gravitational potential energy per molecule can go in some cases up to 1/1000 of the Lennard-Jones energy parameter ε. Finally we reduce the dimensionality of the problem from three to two dimensions, taking into account that although the phase diagram for bidimensional fluids is different from that of the real tridimensional world, nevertheless phase transitions are theoretically possible.[14]

This paper deals with the two liquid phase separation and inmiscibility processes as a function of differences in intermolecular forces of equal and different particles, more precisely, as a function of differences in the Lennard-Jones energy parameters of such interactions.

II METHOD

As sample size we use a bidimensional rectangular region, appropriate for an initial planar triangular lattice of particles. Particle numbers are varied from some runs to the others: 98, 112 and in some quick tests, as few as 49 particles are handled. In the same way particle density goes, as a function of molecular size, from 0.05 to 0.08 particles/Å^2. At the beginning of each run molecules of both kinds are placed randomly in lattice points with velocities taken from a Maxwell–Boltzmann distribution.

The main difficulty lies on the problem of boundary conditions that cannot be periodic in the direction of gravitational field. To solve this, we have used several paths. In some cases lateral periodic boundaries and walls for the vertical direction (that of the field) have been employed; the walls are not rigid, but they represent the average interaction of bulk liquid below the bottom or above the top of the rectangular sample. They act with a Lennard–Jones potential

$$u(z) = 4 \cdot \varepsilon_w \left| \left(\frac{\sigma_w}{z}\right)^{12} - \left(\frac{\sigma_w}{z}\right)^{6} \right| \tag{1}$$

where z is the vertical distance from the wall to any particle, and ε_w and σ_w are selected in such a way they reproduce the previously indicated behaviour. This method is similar to the one used by Rowlinson and coworkers[8] for pure components. In other cases only one attractive wall that of the bottom, is considered, assuming perfect reflection for the top wall placed well above the bulk system (expanding somewhat the sample size). Finally some runs with perfectly reflective walls on top and bottom of the sample have been performed.

The particle interactions follow the 12:6 Lennard–Jones potential expression between i and j molecules

$$u(r_{ij}) = 4\varepsilon_{ij} \left| \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6} \right| \tag{2}$$

The computer program we have developed performs calculations using the straightforward Hamilton formalism of dynamical equation, in such a way the numerical integration works with the first derivatives of momenta and coordinates. We proceed in cartesian coordinates and numerical integration algorithm employed is a combined four order Runge–Kutta–Gill method, followed after few integration steps by the Adams–Moulton predictor-corrector.[15]

The integration time step used has been 0.5×10^{-14} s. Given the initial conditions the system evolves for as long as 3×10^4 or 10^5 time steps. The Verlet bookkeeping device is used as a saving time technique when convenient.

The relative error in energy conservation for 5 × 10^3 steps is less than 0.01%. The simulation gives position and momenta of every particle, Temperature, and potential, kinetic and total energy of the system; finally the three radial distribution functions g_{AA}, g_{BB} and g_{AB} of the A + B mixture are recorded.

III RESULTS

Two different kind of systems, all of them at 0.5 molar fraction, have been studied. The first include real and hypothetical mixtures, generally with notorious differences in the Lennard-Jones parameters of pure components, but following the Lorentz-Berthelot rules for the mixed parameters between unlike molecules

$$\begin{aligned} \varepsilon_{AB} &= (\varepsilon_{AA} \cdot \varepsilon_{BB})^{1/2} \\ \sigma_{AB} &= (\sigma_{AA} + \sigma_{BB})/2 \end{aligned} \tag{3}$$

The second kind is related to situations where those parameters clearly do not behave in such a way, but instead of that, the interaction between unlike molecules is weakened. Both situations favor in practice phase separation as we mentioned before: Notorious differences in the interaction parameters of pure components lead to fluid-fluid inmiscibility[5] and a weak interaction between unlike molecules in other cases, gives origin to phase separation in liquid state.[4]

TABLE I

Lerentz-Berthelot mixtures studied

Components	ε/K(K)	ρ(Å)	m(amu)	$\varepsilon_{BB}/\varepsilon_{AA}$
A	119.8	3.405	10	1
B	119.8	3.405	39.948	
A	59.9	3.405	20.18	2
B	119.8	3.405	39.948	
Ne	35.58	2.740	20.18	3.37
Ar	119.8	3.405	39.948	
A	11.98	3.405	20.18	10
B	119.8	3.405	39.948	

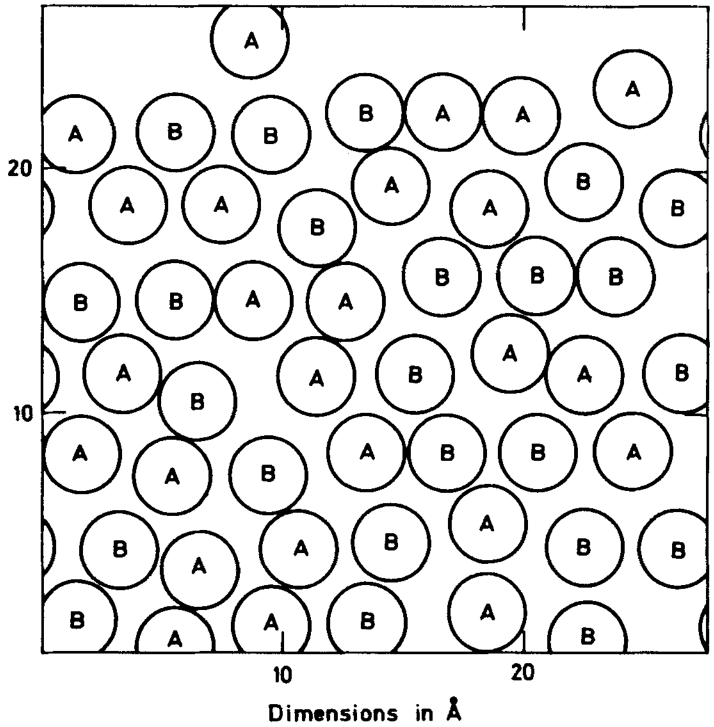

FIGURE 1 Snapshot of the system ($\varepsilon_{\mathrm{AA}} = \varepsilon_{\mathrm{BB}}, m_{\mathrm{A}} = m_{\mathrm{B}}/4$) at $T = 50, 4$ K, after 23000 time steps.

Within the first kind, the systems indicated in Table I have been treated, where always one of the components is Argon ($\varepsilon/K = 119.9$ K, $\sigma = 3.405$ Å and $m = 39{,}948$ amu). In the first system ($\varepsilon_{\mathrm{AA}} = \varepsilon_{\mathrm{BB}}, m_{\mathrm{A}} = m_{\mathrm{B}}/4$) at $T = 50.5$ K, we have tried to see pure gravitational effects in a small sample with walls on top and bottom. As it is apparent from the snapshot of Figure 1 after 23000 time steps, phase separation does not occur, the situation being similar to that of Rotemberg,[16] who failed to separate liquid and solid phases in a system of hard spheres with gravitational field. Gravity action is evident only because it decreases the density in the upper part of the sample.

The second system ($\varepsilon_{\mathrm{AA}} = \varepsilon_{\mathrm{BB}}/2$) with 98 particles and reflective walls, at $T = 49$ K and after 24000 steps exhibits the configuration of Figure 2, where it is easy to observe clusters of each kind of particles. Also the particle density profiles of both components show a predominance of the B component in the middle region of the sample in accordance with the prediction of Mayer and Wood.[17]

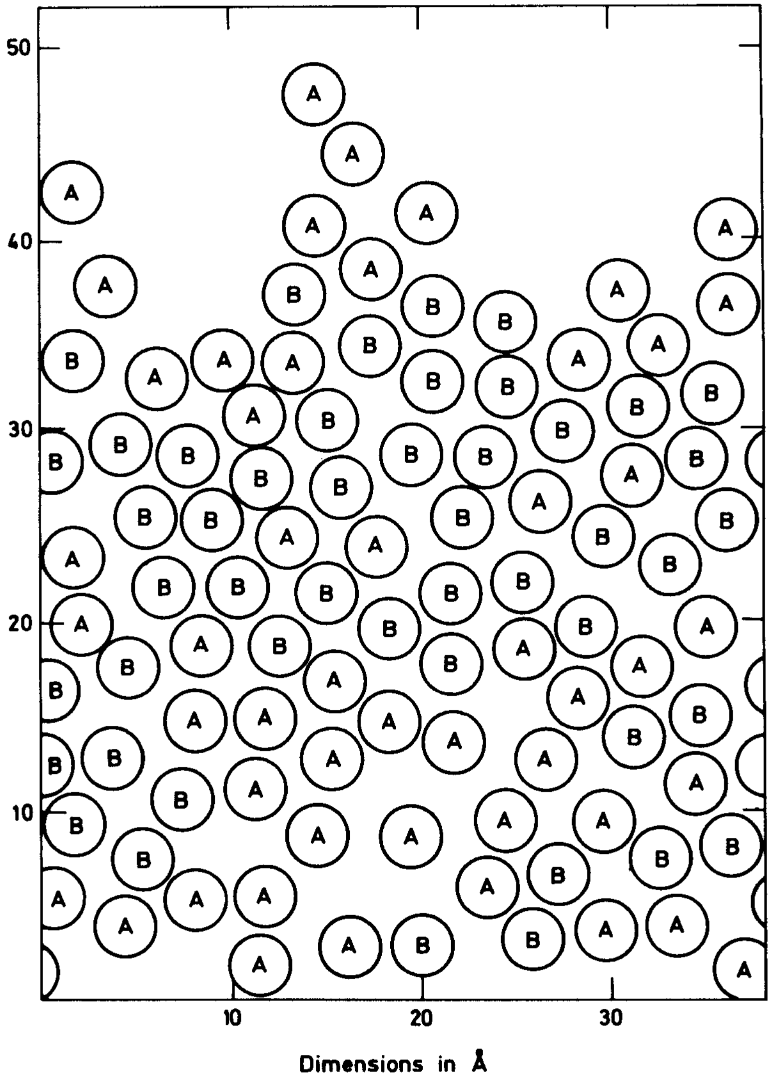

FIGURE 2 Snapshot of the system ($\varepsilon_{AA} = \varepsilon_{BB}/2$) at $T = 49$ K, after 24000 steps.

The situation regarding phase separation is more clear in the third system (Neon + Argon, $\varepsilon_{BB}/\varepsilon_{AA} \simeq 3.4$), studied in several different conditions. Working at $T = 46$ with a very small sample and reflective walls, we obtain the phase distribution of Figure 3, that agrees exactly with the ideas of Mayer and Wood.[17] The system has also been studied with 112 particles and atractive walls, at two different densities and Temperatures. The first run ($\rho = 0.080$

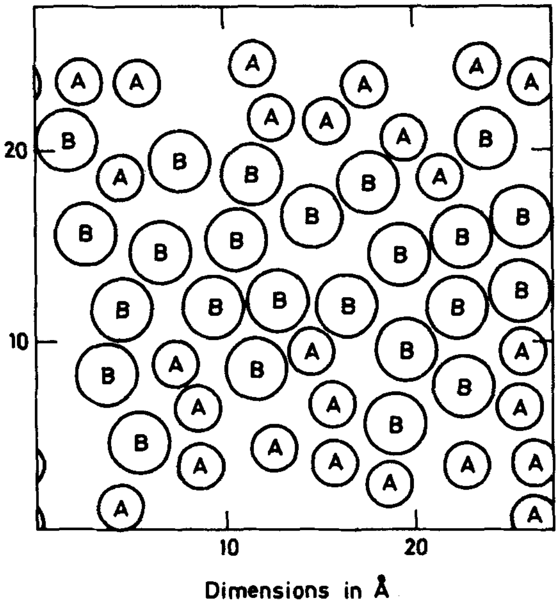

FIGURE 3 Snapshot of the system Ne + Ar at $T = 46$ K, after 11600 cycles.

particles/Å and $T = 54$ K) after 90000 steps shows the radial distribution functions of Figure 4. In a similar way the behaviour of the system in the last run ($\rho = 0.061$ particles/Å^2 and $T = 47$ K) after 120000 steps is summarized in Figure 5. The distribution functions indicate, in both cases, strong interactions between like molecules and, consequently, reduction in the number of contacts between the unlike ones. The situation is similar to the Molecular Dynamics results of Mo *et al.*[18] for the system Krypton + Argon where the relation $\varepsilon_{\mathrm{Kr}}/\varepsilon_{\mathrm{Br}}$ is only 1.4; in our case the first maximum of g_{AB} is clearly smaller than those of g_{AA} and g_{BB}, the reason being the stronger difference between energy parameter of pure components.

Finally the system $\varepsilon_{\mathrm{BB}}/\varepsilon_{\mathrm{AA}} = 10$ has been treated, the main characteristics of the results indicating the location of the B component molecules in the middle of the sample surrounded by molecules of A component in a similar way to Figure 3.

For situations where the Lorentz–Berthelot rules are not obeyed, the systems of Table II have been studied. The first one ($\varepsilon_{\mathrm{AA}} = \varepsilon_{\mathrm{BB}} = 10\varepsilon_{\mathrm{AB}}$) gives the snapshot of Figure 6 after 13400 steps, where phase separation is clear.

The second system is similar to $CH_4 + CF_4$, but with $\varepsilon_{\mathrm{AB}} = (\varepsilon_{\mathrm{AA}} \cdot \varepsilon_{\mathrm{BB}})^{1/2}/2$. The real system $CH_4 + CF_4$ presents an upper consolute temperature at 94.5 K and 0.43 molar fraction of CF_4. In our calculation, where the bottom

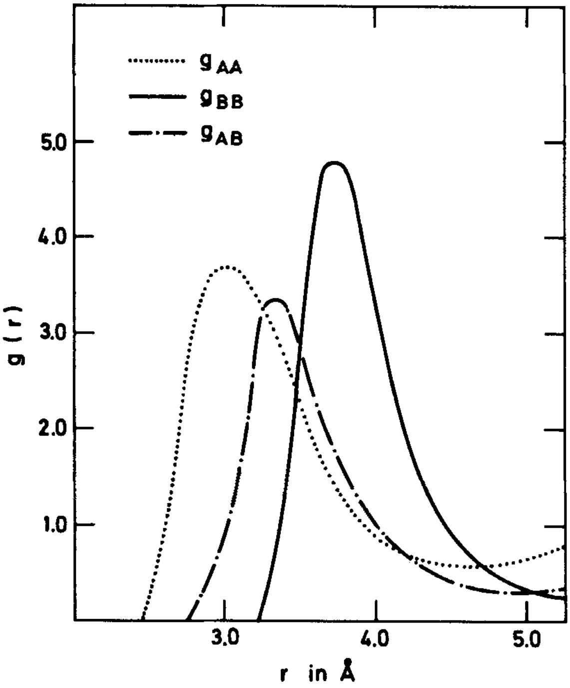

FIGURE 4 Radial distribution functions of the system Ne + Ar at $\rho = 0.080$ particles/Å and $T = 54$ K, after 90000 cycles.

of the sample behaves as an attractive wall and the top as a reflective one, the results at $T = 74$ K after 60000 cycles appear in Figure 7. In this case, apart from phase separation, the spatial disposition of both components (CF_4 in the lower part and CH_4 in the upper one) seems to be a gravity effect. Nevertheless considering the gravity needs a tremendous amount of time to be noted,[13] such effect has to be adscribed mostly to the influence of the attractive wall placed in the bottom of the sample.

IV DISCUSSION

We have shown that, in general, Molecular Dynamics calculation is a useful method to study the problem of fluid miscibility and phase separation as a function of molecular interaction. In fact, it has been proven that in cases where $\varepsilon_{BB}/\varepsilon_{AA} > 2$ or $\varepsilon_{AB} \ll (\varepsilon_{AA} \cdot \varepsilon_{BB})^{1/2}$ phase separation takes place.

A very difficult problem to handle is the question of gravity action. In order the gravity to be effective, it is necessary to eliminate the surface

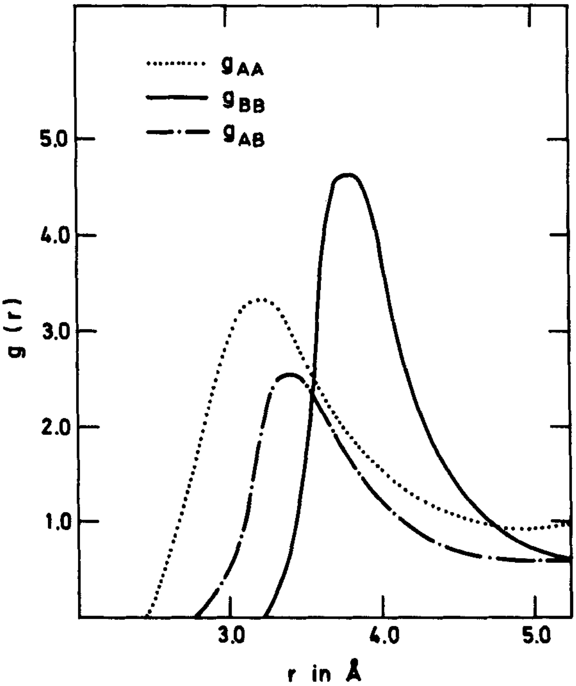

FIGURE 5 Radial distribution functions of the system Ne + Ar at $\rho = 0.061$ particles/Å and $T = 47$ K, after 120000 steps.

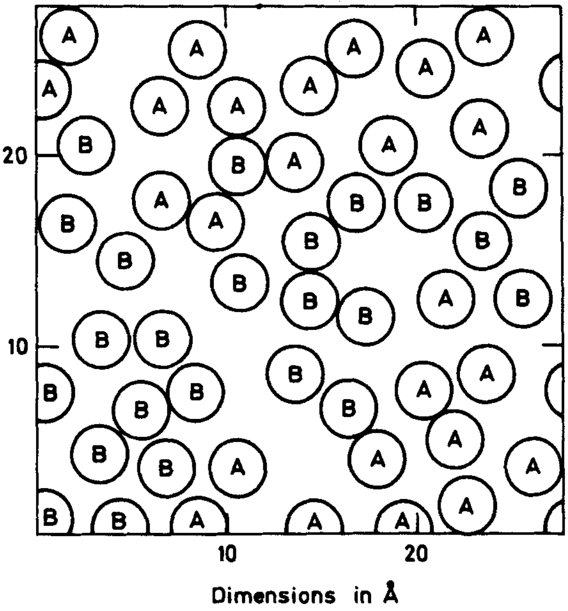

FIGURE 6 Snapshot of the system ($\varepsilon_{AA} = \varepsilon_{BB} = 10\varepsilon_{AB}$) after 13400 steps.

TABLE II

Non Lorentz–Berthelot mixtures studied

Components	ε/K(K)	δ(Å)	m(amu)	ε_{AB}
A	119.8	3.405	39.948	11.98
B	119.8	3.405	39.948	
CH_4	139.0	3.822	16	70.10
CF_4	141.4	4.747	92	

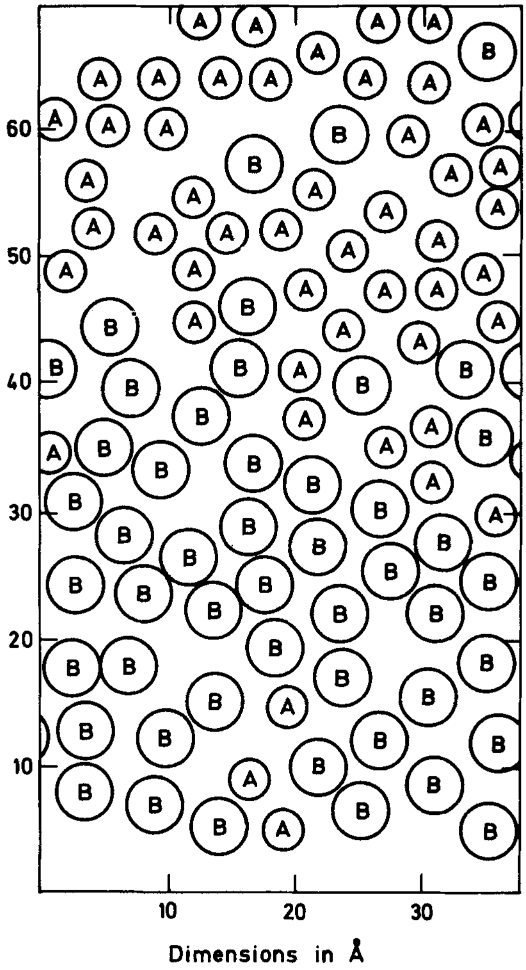

FIGURE 7 The CH_4 + CF_4-like system after 60000 cycles.

tension using boundary condition with attractive walls as described before. Apart from that, gravity to produce barotropic effects clearly observable would require around 10^{-6} s,[13] what is far beyond the actual capacity of simulation by computer methods. Nevertheless this external field is unable, as we pointed out in the example of Figure 1, to produce phase separations, its action being limited to arrange by density the phases already existing. As a consequence, after seeing its behaviour in some cases, it would be convenient, in future work, to eliminate both the gravity field and the special boundary conditions that it imposes.

The source of phase separation lies on the relation of intermolecular forces between particles. Our results agree with the experimental results of systems such as Ne + Ar, He + Xe, Ne + Kr, etc, where $\varepsilon_{BB}/\varepsilon_{AA} > 3$, and with those like $CH_4 + CF_4$ where the interaction between unlike molecules is more weak than that of the pure components.

References

1. B. J. Alder; *J. Chem. Phys.*, **40**, 2724 (1964).
2. M. Rigby, B. J. Alder, A. M. Sapse, and C. E. Hecht, *J. Chem. Phys.*, **52**, 3665 (1970).
3. J. S. Rowlinson: *Liquids and liquid mixtures.* Butterworths, London, 1959.
4. N. Thorp and R. L. Scott, *J. Phys. Chem.*, **60**, 670 (1956); I. M. Croll and R. L. Scott, *J. Phys. Chem.*, **62**, 954 (1958).
4. N. Thorp and R. L. Scott, *J. Phys. Chem.*, **60**, 670 (1956); I. M. Croll and R. L. Scott, *J. Phys. Chem.*, **62**, 954 (1958).
5. W. B. Streett, *J. Chem. Phys.*, **46**, 3282 (1967). W. B. Streett, *J. Chem. Phys.*, **42**, 500 (1964). J. de Swaan Aons and G. A. M. Diepen, *J. Chem. Phys.*, **44**, 2322 (1966). W. B. Streett, *Trans. Faraday. Soc.*, **65**, 696 (1969). N. J. Trappeniers and J. A. Schouten, *Phys. Lett.*, **27A**, 340 (1968).
6. J. R. McDonald, *Mol. Phys.*, **23**, 41 (1972). J. V. L. Singer and K. Singer, *Mol. Phys.*, **24**, 357 (1972).
7. G. M. Torrie and J. P. Valleau, *J. Chem. Phys.*, **66**, 1402 (1977). C. Hoheisel, *Ber. Bunsenges*, **81**, 462 (1977). K. Toukubo and K. Nakanishi, *Ber. Bunsenges*, **81**, 1046 (1977). C. Hoheisel and U. Deiters, *Mol. Phys.*, 37, 95 (1979); C. Hoheisel, *Phys. Chem. Liq.*, **9**, 245 (1980).
8. A. C. L. Opitz, *Phys. Lett.*, **47A**, 439 (1974). J. K. Lee, J. A. Barker, and G. M. Pound, *J. Chem. Phys.*, **60**, 1976 (1974). K. S. Lin, *J. Chem. Phys.*, **60**, 4226 (1974). F. F. Abraham, D. E. Schereiber, and J. A. Barker, *J. Chem. Phys.*, **62**, 1958 (1975). J. Miyazaki, J. A. Barker, and G. M. Pounel, *J. Chem. Phys.*, **64**, 3364 (1976). M. Rao and D. Levesque, *J. Chem. Phys.*, **65**, 3233 (1976). G. A. Chapela, G. Saville, and J. S. Rowlinson, *Faraday Disc. Chem. Soc.*, **59**, 22 (1975). S. M. Thompson, *Faraday Disc. Chem. Soc.*, **66**, (1978).
9. G. A. Chapela, G. Saville, and J. S. Rowlinson, *J. Chem. Soc. Faraday Trans. II*, **73**, 1133 (1977).
10. G. Scheider: *Ber Bunsenges*, **70**, 497 (1966). R. L. Scott: *Ber Bunsenges*, **76**, 296 (1972).
11. W. G. Hoover and W. T. Ashurst: Non equilibrium molecular dynamics, in *Theoretical Chemistry Vol. 1.* Ed. H. Eyring and D. Henderson, Academic Press. N.Y. 1975.
12. B. E. Sundquist and R. A. Oriani, *J. Chem. Phys.*, **36**, 2604 (1962). R. B. Heady and J. W. Cahn, *J. Chem. Phys.*, **58**, 896 (1972). C. Y. Mou and R. Lovett, *J. Chem. Phys.*, **62**, 3298 (1975). W. H. Zurek and W. C. Schieve, *J. Chem. Phys.*, **68**, 840 (1978).
13. T. E. Block, E. Dickinson, C. M. Knobler, V. N. Schumaker, and R. L. Scott, *J. Chem. Phys.*, **66**, 3786 (1977); M. Giglio and A. Vendramini, *J. Chem. Phys.*, **68**, 2016 (1978); C. M. Knobler and R. L. Scott, *J. Chem. Phys.*, **68**, 2017 (1978).

14. D. Ruelle, *Phys. Rev. Lett.*, **27**, 1040 (1971). J. L. Lebowitz and E. H. Lieb, *Phys. Lett.*, **39A**, 98 (1972); M. E. Fisher: Phase transition, Symmetry and dimensionality, in *Essay in Physics*. Vol. 4. Ed. G. K. T. Conn and G. N. Fowler, Academic Press, London 1972; S. Toxwaerd, *J. Chem. Phys.*, **62**, 1589 (1975).
15. D. L. Bunker, *Method. Comput. Phys.*, **10**, 287 (1971).
16. A. Rotemberg, New York University Report NYO–1480–3 (1964); A. Rotemberg, *J. Chem. Phys.*, **43**, 4377 (1965).
17. J. E. Mayer and W. W. Wood, *J. Chem. Phys.*, **42**, 4268 (1965).
18. K. C. Mo, K. E. Gubbins, G. Jacucci, and I. R. McDonald, *Mol. Phys.*, **27**, 1173 (1974). I. R. McDonald and K. Singer, *Chemistry in Britain*, **9**, 54 (1973).